ERDC/CRREL TR-05-13

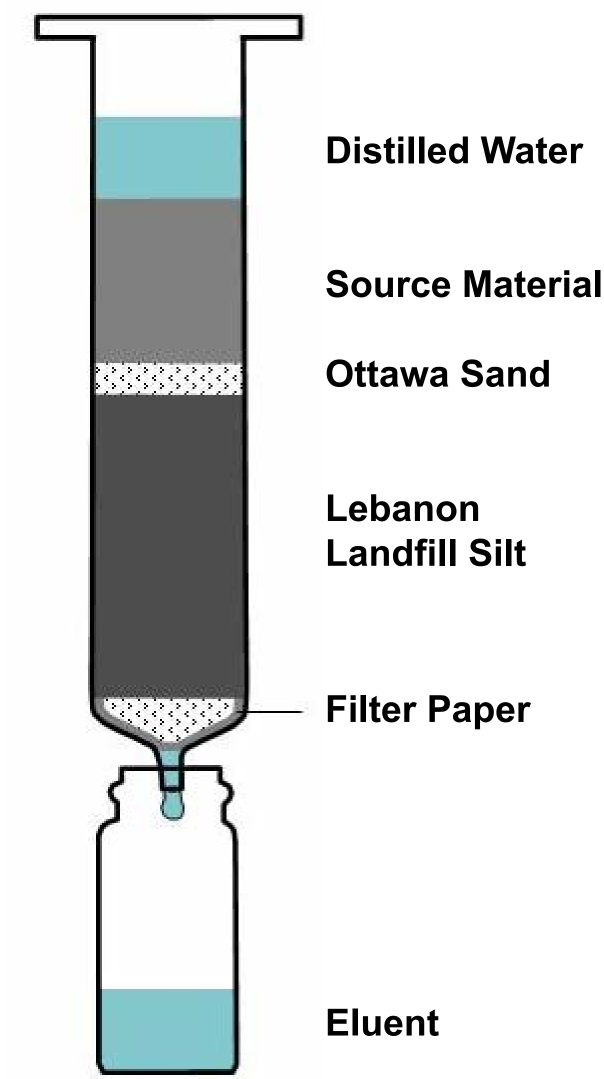
Cold Regions Research and Engineering Laboratory

US Army Corps of Engineers®
Engineer Research and Development Center

Elution of Energetic Compounds from Propellant and Composition B Residues

Alan D. Hewitt and Susan R. Bigl

July 2005



COVER: Schematic of elution column investigation setup.

ERDC/CRREL TR-05-13
July 2005

Elution of Energetic Compounds from Propellant and Composition B Residues

Alan D. Hewitt and Susan R. Bigl

Engineer Research and Development Center
Cold Regions Research and Engineering Laboratory
72 Lyme Road
Hanover, New Hampshire 03755

Prepared for U.S. ARMY ENVIRONMENTAL CENTER

ABSTRACT

Surface soils from two firing points, an artillery impact range, and soils fortified with propellants were evaluated in column elution experiments assessing the release of energetic compounds from melt-cast crystalline explosives and nitrocellulose-based polymeric propellant formulations. Soils obtained from active military ranges were collected at locations identified as potential source zones for energetic residues. The laboratory columns contained 30 g of a silty-sand loam beneath 5.0 g of soil laden with energetic compounds. For 10 or 12 consecutive days, 10 mL of water was eluted through each of the columns. HMX, RDX, and TNT were quickly leached from a soil laden with Composition B residues that had been obtained where an artillery projectile had partially detonated. In contrast, neither 2,4-DNT nor NG were readily released from surface soils laden with propellant residues deposited from the firing of 105-mm howitzers and Light Anti-Armor Weapons (LAW), respectively. A soil prepared by grinding pieces of 105-mm howitzer and LAW rocket propellants with a sand matrix released much greater concentrations of 2,4-DNT and NG than residue-laden soils from firing points. Both the composition of energetic formulations (crystalline vs. polymeric) and physical state of propellant residues deposited at firing points play important roles in the fate and transport of energetic compounds.

CONTENTS

ILLUSTRATIONS

TABLES

PREFACE

This report was prepared by Alan D. Hewitt, Research Physical Scientist, Environmental Sciences Branch (ESB), U.S. Army Engineer Research and Development Center (ERDC), Cold Regions Research and Engineering Laboratory (CRREL), Hanover, New Hampshire; and by Susan R. Bigl, Research Physical Scientist, Geophysical Sciences Branch (GSB), ERDC-CRREL.

Funding for this work was provided by the U.S. Army Environmental Center (USAEC), Martin H. Stutz, Project Monitor.

Jay L. Clausen and Dr. Thomas F. Jenkins, ESB, CRREL, provided technical reviews.

This report was prepared under the general supervision of Antonio J. Palazzo, Acting Chief, Environmental Sciences Branch, CRREL; Dr. Richard M. Detsch, Chief, Geophysical Sciences Branch, CRREL; Dr. Lance D. Hansen, Deputy Director, CRREL; and James L. Wuebben, Acting Director, CRREL.

The Commander and Executive Director of the Engineer Research and Development Center is Colonel James R. Rowan, EN. The Director is Dr. James R. Houston.

Elution of Energetic Compounds from Propellant and Composition B Residues

ALAN D. HEWITT AND SUSAN R. BIGL

1 INTRODUCTION

Over the last five years, numerous investigations of active military firing ranges have been undertaken to determine the near-surface burden of energetic residues (Jenkins et al. 2001; Pennington et al. 2001–2004; Walsh et al. 2001, 2004, 2005). The need to fulfill this data gap was in response to the discovery of RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) in the groundwater at Massachusetts Military Reservation on Cape Cod and the subsequent regulatory action that curtailed live-fire training (U.S. EPA 2000). Investigations at the active training ranges were intended to assess the current conditions, identify potential source areas, and provide recommendations to help sustain military training and testing activities. Some initial findings were that energetic residues and their concentrations are dependent on the training activity, and representative characterization requires a well-developed sampling plan and strategy.

Explosives detected most frequently during these site investigations have been TNT (2,4,6-trinitrotoluene), RDX, HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), NG (nitroglycerin), 2,4-DNT (2,4-dinitrotoluene), and the environmental transformation products of TNT: 2ADNT (2-amino-4,6-dinitrotoluene), 4ADNT (4-amino-2,6-dinitrotoluene), and 1,3,5-TNB (1,3,5-trinitrobenzene) (Jenkins et al. 2001; Pennington et al. 2001–2004; Walsh et al. 2001, 2004, 2005). Overall, the compounds frequently found on impact ranges are TNT, RDX, HMX, and the breakdown products of TNT; those found at firing points are 2,4-DNT and NG. Concentrations of these energetic residues decrease rapidly with depth in the soil profile and with distance from the firing position and target locations. As a consequence, the characterization of potential source areas for ground and surface water contamination has focused on locations where the training activities are the heaviest and where munitions have ruptured or partially detonated, dispersing chunks of energetic residues.

Concurrent with training range investigations, studies were performed to assess the mass and physical characteristics of energetic residues not consumed during live-fire or blow-in-place detonations (Jenkins et al. 2000a,b; Hewitt et al. 2003; Taylor et al. 2004; Walsh et al. 2005). This effort has established that energetic residues are dispersed into the environment as particles of various sizes and shapes at the location where munitions are fired (projected) and where they detonate.

Dispersion of energetic residue particulates at firing positions and in impact ranges has confounded efforts to establish representative mean concentrations, since both compositional and distributional heterogeneity must be adequately addressed. Investigations have found that multi-increment sampling strategies limit these sources of variability and achieve an acceptable level of uncertainty for establishing the mean concentration of energetic residues at firing positions and on small impact ranges, e.g., anti-armor and hand grenade (Jenkins et al. 2004a, 2004b, 2005; Walsh et al. 2005). Combined judgmental sample location selection and proper sampling strategy has allowed representative samples to be collected from areas on military training and testing facilities where energetic residues are likely to build up to levels of environmental concern. Energetic residues within the top few cm of surface soils frequently range between 10 and 10,000 mg/kg at heavily used firing points and in close proximity to rounds that have ruptured or partially detonated (Jenkins et al. 2001; Pennington et al. 2001–2004; Walsh et al. 2001, 2004, 2005).

Laboratory column studies have been performed to assess the migration of RDX, TNT, and other energetic materials through soil (e.g., Kayser and Burlinson 1988; Selim and Iskandar 1994; Pennington et al. 1995). However, information with respect to the migration of energetic compounds associated with propellants is not readily available to the general public.* Energetic compounds that are melt-cast (e.g., TNT and RDX) form crystalline materials. Their rate of dissolution is dependent on the composition of the formulation and size of the particles (Brannon and Pennington 2002). When manufacturing propellants M1 and M7, NG and 2,4-DNT, respectively, are combined with nitrocellulose (NC) and other materials. NC is a water-insoluble polymer that retains these two compounds when unconsumed in the process of launching a projectile (Walsh et al. 2005). The condition in which these energetic compounds exist on training ranges may have a pronounced influence on their rate of dissolution, and therefore their availability for migration to groundwater or runoff to surface water bodies.

* Personal communication, J.L. Clausen, ERDC-CRREL, 2005.

2 OBJECTIVE

This study will evaluate release of energetic compounds from soils with high energetic residue concentrations that were collected on active training ranges. It will utilize multi-increment samples collected behind an anti-armor weapons firing position, near a heavily used 105-mm howitzer firing position, and on an impact range where an artillery projectile had partially detonated. It also will investigate laboratory-prepared samples fortified with known source amounts of propellant chemicals to assess whether they mimic those obtained from a firing range.

3 MATERIALS AND METHODS

Propellant Composition

Individual 105-mm howitzer propellant grains (1.1 ± 0.1 g) and small pieces (0.2 ± 0.01 g) of propellant removed from a large chunk recovered from an anti-tank range were extracted with acetone to estimate the amount of energetic compounds present. The structural composition of these two propellants was completely broken down after several days of extraction with intermittent shaking; however, the solutions remained cloudy, indicating that NC polymer wasn't completely dissolved.

Aqueous Dissolution of Propellant Compositions

Three propellant grains from a 105-mm howitzer cartridge and three pieces (0.52 ± 0.03 g) of rocket propellant from an anti-tank training range were separately immersed in 40 mL of reagent-grade water in glass vials with Teflon-lined septa caps. After submersion, aliquots were removed with volumetric pipettes periodically over the next few weeks to assess the rate and extent of dissolution of 2,4-DNT and NG.

Column Experiments

Soil columns were constructed of layers of soil held in the barrel of a 60-mL plastic syringe. Air-dried Lebanon Land Fill (LLF) soil was sandwiched between a thin upper and lower layer of Ottawa coarse sand and topped with soil containing residues of energetic compounds. The LLF soil is classified as a silty-sand (50% silt-clay and 45% fine sand), and contains approximately 0.5% organic matter. Prior to pouring 30 g of the LLF soil into a syringe, a 13-mm glass fiber filter was placed over the nozzle, wetted with reagent-grade water, and then covered evenly with 2.5 g of Ottawa sand. After transferring, the LLF soil was compacted to a volume of 22 cm^3 (density 1.36 g/cm^3). To separate the column from the source soil or control, 2.5 g of Ottawa sand was evenly spread over the LLF soil. The final upper portion of the column was either 5.0 g of source material containing energetic compounds or the control. The source materials and control were first air-dried and sieved through a #10 mesh sieve. The 5.0-g subsample was built by obtaining 15 or more increments of the sieved < 2-mm size fraction. The following source materials were used:

a) Surface soil from Fort Hood that was collected at the bottom of a crater containing several large pieces (chunks) of Composition B (60% RDX

and 39% TNT). The energetic residues were most likely from the partial detonation of an 81-mm mortar round. Military-grade RDX contains about 10% HMX as an artifact of manufacturing.

b) Surface soil collected behind the firing point at an anti-tank range on Canadian Force Base Valcartier (CFB-Valcartier). The energetic residues present at this site were from a double-based propellant used with the 66-mm M72 LAW rocket (Jenkins et al. 2004a).

c) Surface soil collected 5 m from the muzzle break on the right side of a 105-mm howitzer gun position at Fort Lewis, Washington. Surface samples collected near 105-mm howitzer firing positions have been shown to contain 2,4-DNT, which is consistent with the single-base propellant formulation used for this weapon (Jenkins et al. 2001; Walsh et al. 2001, 2004, 2005; Hewitt and Walsh 2003).

d) Small pieces cut from a chunk of rocket propellant with a razor blade. The propellant chunk was unconsumed 66-mm M72 LAW rocket fuel. The small pieces of propellant were ground for 60 seconds with 100 g of commercial sand in a Model LM2 Laboratory Ring Mill (LabTech Essa Pty. Ltd., Bessendean, WA, Australia).

e) Small pieces cut from a 105-mm howitzer single-based propellant grain with a razor blade. The small propellant pieces were ground for 60 seconds with 100 g of commercial sand in a Model LM2 Laboratory Ring Mill (LabTech Essa Pty. Ltd., Bessendean, WA, Australia).

f) A control prepared with 5.0 g of soil free of energetic compounds.

For the surface soils obtained from active training ranges (sources a, b, and c), three replicate columns were prepared and treated. Triplicate setups were used for these residue-laden soils because they were not ground and it was likely that particles of energetic residues would not be uniformly mixed throughout the sample. Therefore, the 5.0-g subsamples taken for the column source material would have variable amounts of energetic residues (Walsh et al. 2002, Hewitt and Walsh 2003). Only a single column was prepared and treated for the remaining (source d, e, and f) soils. These materials had either been ground to a fine powder or served as a control and contained no energetic compounds. All of the column studies were performed in a laboratory with no windows and the lights remained off except to collect aliquots of the column eluent.

To limit channeling through the columns, they were saturated with water by submersing the tip of the soil-packed syringe into reagent-grade water. When the watermark reached the top of the LLF, the syringe was removed. It took approxi-

mately 45 minutes to fill the column pore volume with 11.1 ± 0.2 mL of reagent-grade water.

Once the LLF was saturated, 10 mL of reagent-grade water was gently poured onto the top of the column (source portion) and a 20-mL scintillation vial placed beneath the nozzle. A head of water existed for about six hours and effluent continued to elute from the nozzle for about 10 hours. Every 24 hours, the vial was replaced with a new one and 10 mL of reagent-grade water was added to the top of the column. This cycle was repeated for at least 10 consecutive days. The amount of column effluent obtained each day was measured by weighing the vial before and after each daily collection.

After the experiment was completed, the saturated soils were recovered with a clean stainless-steel spatula. Each column was separated into the following media portions: the source or control layer, and the top, middle, and bottom third of the LLF soil. Special care was taken to remove all of the source portion and most of the Ottawa sand separating it from the LLF soil. Each portion was transferred directly to a 40-mL VOA vial and extracted with 20 mL of acetonitrile overnight in a water-cooled sonic bath.

RP-HPLC Analysis

The aqueous phase from the propellant dissolution experiment and the effluent from the column experiments were prepared for analysis by transferring 0.300 mL or a measured smaller volume, then combining it with an appropriate amount of reagent-grade water for a final volume of 0.900 mL and adding 0.300 mL of acetonitrile. Solvent extracts of the propellant formulations and soil samples were prepared by passing the extract through a 0.45-µm Millex FH filter. This filtered extract or a further dilution of the extract with acetonitrile was mixed one part solvent with three parts reagent water. RP-HPLC-UV analysis was performed following the general guidelines provided in Method 8330 (U.S. EPA 1994) on a modular system from Thermo Finnigan composed of a Spectra-SYSTEM model P1000 isocratic pump, a model AS300 auto-sampler, and a model UV2000 dual-wavelength absorbance detector set at 210 and 254 nm. The HPLC separations were performed on a 15-cm × 3.9-mm (4-µm) Nova Pac C_8 (Waters Millipore) column eluted with 1.4 mL/minute 15:85 isopropanol:water at 28°C. Table 1 presents the practical quantitation limits for this system and sample preparation protocol.

Table 1. Practical quantitation limits (PQLs) for selected energetic residues in soil and water.

Analyte	RP-HPLC	
	Soil (µg/kg)	Water (µg/L)
HMX	26	13
RDX	34	17
TNT	16	8
2,6-DNT	19	10
2,4-DNT	28	14
2ADNT	38	19
4ADNT	32	16
NG	20	10

4 RESULTS AND DISCUSSION

Propellant Composition

An initial task was to establish the composition of the range propellant sources. Analysis of the acetone extracts of the two propellants indicated that the 105-mm howitzer propellant grains were 9.3% by weight 2,4-DNT and the propellant found on the anti-tank range was 31% by weight NG. Based on these findings and referencing the Midas database, the 105-mm howitzer propellant was composition M1, a single-base propellant composed of 85% NC, 9% 2,4-DNT, 5% dibutylphthalate, and 1% diphenylamine. The rocket propellant obtained on the anti-tank range was most likely composition M7, a double-based propellant composed of 54.6% NC, 35.5% NG, and 7.8% potassium perchlorate. Henceforth, the 105-mm howitzer propellant residues also will be referred to as the M1 composition, and the propellant residues from the LAW rocket training range will be assumed to be M7 composition.

Aqueous Dissolution of Propellant Compositions

When grains or small pieces of the M1 and M7 propellants were submersed in reagent-grade water, the 2,4-DNT and NG present in these polymeric matrices, respectively, dissolved into the aqueous phase. Figure 1 depicts the increase in dissolved concentrations with time. After 10 days of dissolution, concentrations of 2,4-DNT and NG were, respectively, approximately 1/100 and 1/5 of their solubilities (Table 2). The mass of 2,4-DNT and NG in solution after 10 days amounts to approximately 0.9% and 7.4% of the mass present in the M1 and M7 propellants, respectively. These findings suggest that NG is more readily leached from the M7 polymer matrix than the 2,4-DNT from the M1. Possible explanations for this difference are that NG has a greater solubility than 2,4-DNT; the propellant chunk recovered from the anti-tank range had been weathered; or NC has a greater affinity for 2,4-DNT.

Column Experiments

The concentrations of energetic compounds determined for the source materials for the column experiments are presented in Table 3. No detectable energetic compounds were present in the control soil and the LLF loam used in all of the columns. As anticipated, analyte concentrations for the subsample triplicates of the three range samples had greater variation than the laboratory-prepared source materials. The range soils were air-dried and sieved, but were

not ground prior to subsampling. Therefore, the size of energetic residue particles in the field samples was limited only to < 2 mm in diameter. The two laboratory-prepared source materials were ground with sand, reducing the propellant pieces to a fine powder (< 0.075 mm). The percent relative standard deviation of less than 3% suggests the laboratory-prepared samples were well mixed prior to subsampling (Walsh et al. 2004). Table 3 also presents an estimate of the total energetic analyte mass initially present in the source portion of the columns. Concentrations in the daily column effluent collections and the four portions of column media at the end of the experiment are presented in Appendix A.

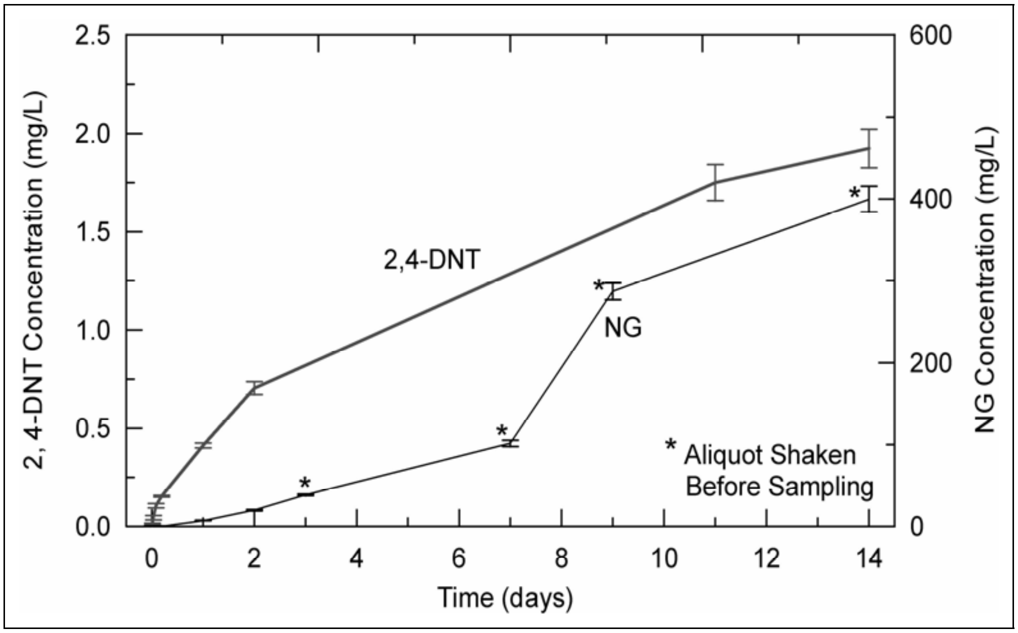


Figure 1. Solution concentration vs. time (days) for propellant submersed in water. Error bars indicate the standard deviation of triplicate treatments.

Composition B

Effluent concentrations resulting from the column experiment that included weathered Composition B source material are presented in Figure 2. The effluent concentrations of HMX and RDX for these experiments consistently exceeded 40% and 70% of their respective aqueous solubilities (Table 2). In contrast, TNT and the two AmDNTs attained only about 21% and 1% of their respective aqueous solubilities (Table 2). Moreover, even though TNT has a greater solubility than RDX, the column effluent RDX concentrations almost always exceeded those of TNT. In general, effluent concentrations of these two compounds are

consistent with the saturated column flow studies of Phelan et al. (2003). However, they typically observed higher concentrations of TNT as compared to RDX. One explanation for this discrepancy is that their column studies used glass beads as a column matrix; therefore, degradation and sorption effects would be diminished compared to soil matrix.

Table 2. Water solubility of selected energetic compounds.

Analyte	Water solubility (mg/L)
TNT	130 @ 20°C
RDX	42 @ 20°C
HMX	5.0 @ 25°C
2AmDNT	2800
4AmDNT	2800
2,4-DNT	270 @ 22°C
NG	1500 @ 20°C

Table 3. Energetic residue concentrations (mg/kg) in triplicate subsamples of the different source materials.

	Concentration (mg/kg)				
	HMX	RDX	TNT	2AmDNT	4AmDNT
a. Field Composition B					
Mean	129	1160	367	6.5	7.1
Total mass*	(645)	(5800)	(1840)	(32)	(36)
Std Dev	33.6	238	202	0.1	0.1
RSD (%)	26%	21%	55%	1.5%	1.4%

	b. NG (mg/kg)		c. 2,4-DNT (mg/kg)	
	Field	Laboratory	Field	Laboratory
Mean	1770	1237	40	505
Total mass*	(8850)	(6180)	(200)	(2520)
Std Dev.	330	25.2	32.8	5.03
RSD (%)	18.6%	2.0%	82%	1.0%

* Estimate of mass (μg) of energetic compound in 5.0 g of soil.

Note: No energetic residues were detected above their PQLs in either the control or the LLF soils.

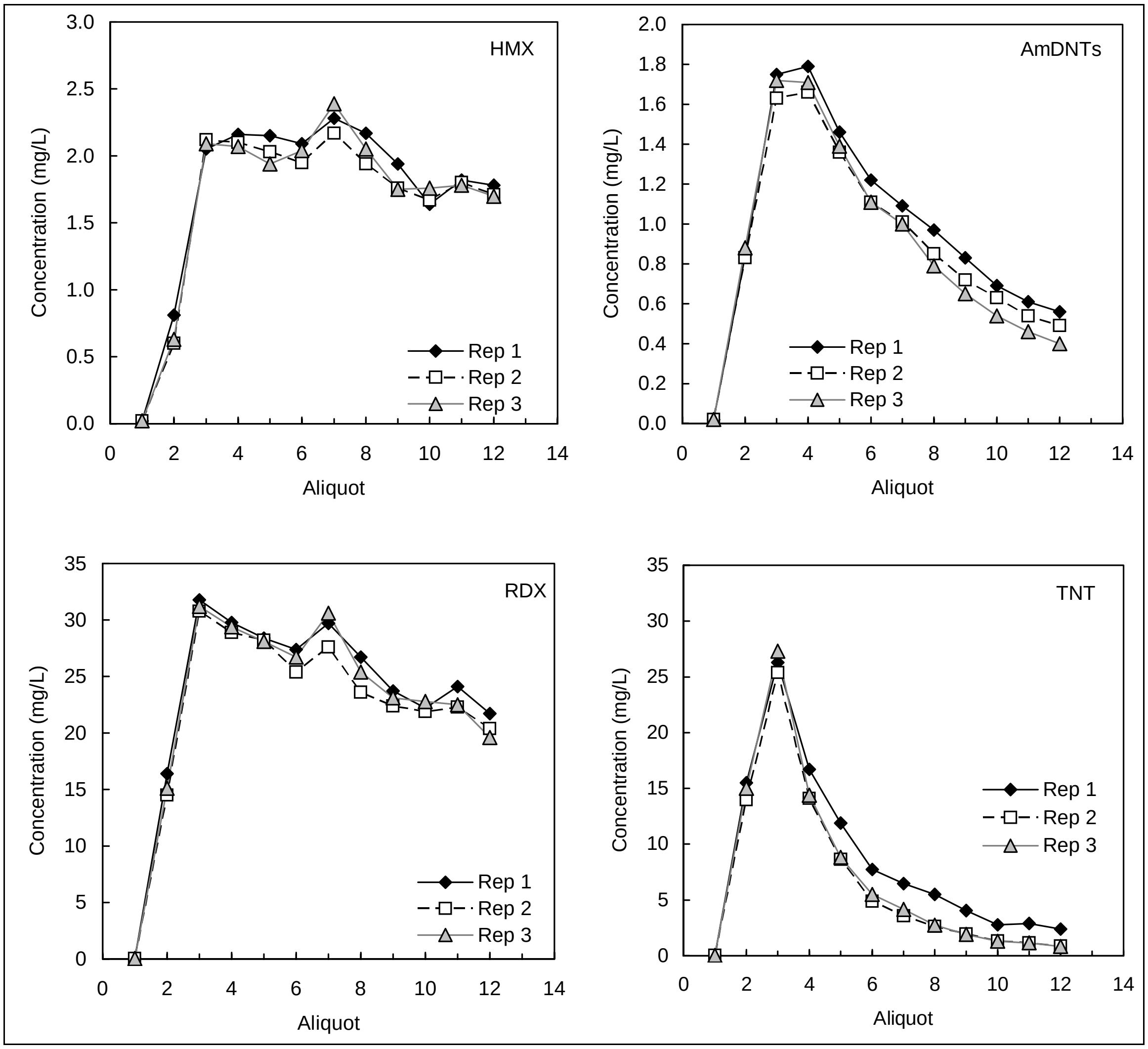


Figure 2. Effluent concentrations (mg/L) from column with Composition B residue source soil.

Two observed patterns in the effluent concentrations were a much greater decrease in TNT and the AmDNTs relative to HMX and RDX over the course of the experiment, and the HMX maxima was achieved a couple days later than the RDX maxima. The first trend suggests there was increased microbial activity after a couple of days, making less of the TNT and AmDNTs available for leaching. This trend is consistent with degradation of TNT and the subsequent sorption of this compound onto soil matrices (Pennington et al. 1995, Major 1999). The second trend, a slight HMX maximum, that occurred for the seventh aliquot (day 7) can likely be attributed to solubility. Lower solubility of HMX

results in slower dissolution and causes enrichment compared to RDX in surface soils. This weathering enrichment phenomenon has been observed for range soils containing RDX residues (Jenkins et al. 2004a, 2004b, 2005).

Table 4. Composition B residue source soil. Mass (µg) of energetic compounds in column effluent and portions of column media.

Sample	Portion	Mass (µg)				% of total recovery			
		HMX	RDX	TNT	AmDNTs	HMX	RDX	TNT	AmDNTs
	Total source mass*	640	5800	1800	68				
Replicate 1	Effluent	203	2732	986	114	26.5%	39.1%	58.6%	78.5%
	Source	538	4020	672	26.6	70.2%	57.5%	39.9%	18.3%
	Top-LLF	12.4	88	8.4	2.5	1.6%	1.3%	0.5%	1.7%
	Middle-LLF	7.3	79.2	8.98	1.14	1.0%	1.1%	0.5%	0.8%
	Bottom-LLF	6.04	70.6	8.16	1.02	0.8%	1.0%	0.5%	0.7%
	Total recovery	767	6990	1680	145				
	% rec of est source†	120%	121%	94%	214%				
Replicate 2	Effluent	193	2577	750	105	32.5%	49.0%	89.2%	78.7%
	Source	372	2460	82.2	23.2	62.6%	46.8%	9.8%	17.4%
	Top-LLF	16.80	80.2	3.06	2.14	2.8%	1.5%	0.4%	1.6%
	Middle-LLF	6.22	68	2.88	0.92	1.0%	1.3%	0.3%	0.7%
	Bottom-LLF	6.44	74	2.98	2.11	1.1%	1.4%	0.4%	1.6%
	Total recovery	594	5260	841	133				
	% rec of est source	93%	91%	47%	196%				
Replicate 3	Effluent	196	2662	795	103	35.7%	45.6%	94.6%	76.8%
	Source	328	2900	42.2	25	59.7%	49.7%	5.0%	18.6%
	Top-LLF	13.46	138.6	0.8	2.42	2.4%	2.4%	0.1%	1.8%
	Middle-LLF	5.80	61.2	1.1	1.8	1.1%	1.0%	0.1%	1.3%
	Bottom-LLF	6.38	70	1	1.92	1.2%	1.2%	0.1%	1.4%
	Total recovery	550	5830	840	134				
	% rec of est source	86%	101%	47%	197%				

* Estimated mass of energetic compounds in source soil.

† Percent recovery of estimated mass initially present in source soil.

Table 4 shows the mass of the energetic compounds established for the column effluent and the four portions of column media. Also tabulated are the percentages of total effluent and the four media portions relative to the total mass of HMX, RDX, TNT, and AmDNTs recovered for each column. Lastly, the total

amount recovered is compared to the mass estimated to be initially present in the source material. For all three columns, the total mass of AmDNTs recovered far exceeded that estimated to be initially present in the source. In contrast, the total recovered mass of TNT for two columns was much lower than the estimated source. These trends are consistent with the major degradation pathway for TNT (McCormick et al. 1976). The total recovery of RDX and HMX is within ± 20% of the expected source strength, suggesting these compounds were not degraded.

HMX exhibited a twofold decrease in concentration from the top to the bottom of the three LLF sections, suggesting that HMX was attenuated moreso than RDX (Table 4). In this case, the sorption was reversible, which is not necessarily the case for TNT and the AmDNTs, the latter of which can covalently bond to organic matter (Thorne and Leggett 1997). The percentages relative to the total mass recovered show that the greatest amounts of TNT and AmDNTs were present in the effluent; in constrast, most HMX and about half of the RDX was still present in the source portion. Therefore, the amount of TNT available for leaching from this source was almost exhausted, due to dissolution and transformation. On the other hand, effluent concentrations greater than 25% of the solubility of HMX and RDX likely would have continued for several more elution cycles. Overall, the trends observed for this column experiment are consistent with what has been reported for the groundwater plumes at the Massachusetts Military Reservation. Clausen et al. (2004) reported that beneath the impact range, RDX has migrated farther than HMX; TNT and AmDNTs have been found only close to source zones.

M7 Composition: LAW Rocket Propellant from Anti-tank Range

Figure 3 shows the effluent concentrations of NG for the column experiments with the source soil containing propellant residues from anti-tank ranges. Although both elution curves showed the same trend, the dissolution of NG is much greater for the laboratory-fortified soil compared with the surface soil obtained from a firing point of an active range. Maximum NG concentration in the laboratory-fortified soil column was nearly 20% of its solubility; in the range soil columns, NG concentration failed to reach 0.5% solubility (Table 2). Table 5 shows the mass of NG determined for the column effluent and media portions, and the percentages relative to the total mass of NG recovered. The greatest amount of NG was recovered in the effluent for the laboratory-fortified soil; it was not leached from the source in the other columns. One explanation for these differences is that the grinding of pieces of propellant with sand created much greater surface area than was present on the naturally weathered propellant residues that exist at firing points.

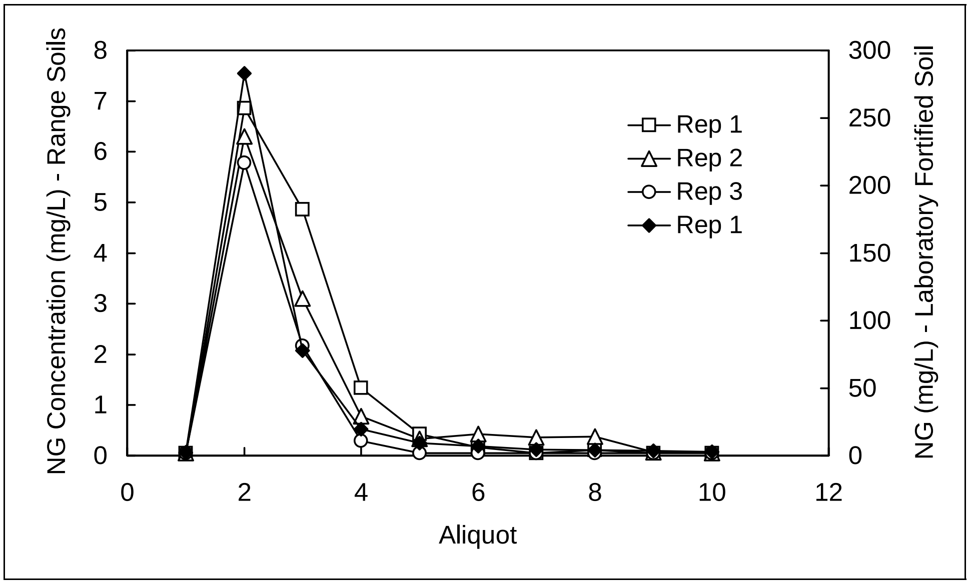


Figure 3. NG effluent concentration (mg/L) from columns with laboratory-fortified (solid diamond) and range (open symbols) source soils contaminating M7 propellant residue.

The fact that 1 to 2% of NG mass was recovered in the effluent of the range soil columns indicates that some migration occurs. This finding is consistent with profile samples collected at the firing point on an anti-tank range. Thiboutot et al. (2004) reported detectable concentrations of NG in profile samples below 60 cm near a fixed firing point. The approximate NG concentrations at the bottom of these soil profiles in front of and behind the firing point were, respectively, 0.01 and 0.2 mg/kg. These subsurface concentrations were about four orders of magnitude below the estimated surface concentrations at these locations. The slow release of NG from propellant residues is one reason for this large decrease in concentration. However, microbiological degradation (Jenkins et al. 2003) and adsorption (Brannon and Pennington 2002; Clausen, personal communication)* also must be considered. Only 83% of the estimated initial source mass of NG was recovered in the laboratory-fortified column experiment (Table 5). A large decrease in mass of NG recovered from the top to the bottom portions of the LLF media was also observed. These trends are likely due to other mechanisms, such as microbiological degradation and adsorption.

* Personal communication, J.L. Clausen, ERDC-CRREL, 2005.

Table 5. M7 residue source soil. Mass (µg) of NG in column eluent and portions of column media.

		Portion	Mass (µg) portion	% of total NG recovery
Sample	Laboratory prepared	Total source mass*	6200	
		Effluent	4060	78.4%
		Source	1050	20.4%
		Top-LLF	46.4	0.9%
		Middle-LLF	6.56	0.1%
		Bottom-LLF	9.46	0.2%
		Total recovery	5180	
		% rec of est source†	83%	
Range soil	Replicate 1	Est. source mass	8850	
		Effluent	133	1.6%
		Source	8000	95.1%
		Top-LLF	258	3.1%
		Middle-LLF	16.5	0.2%
		Bottom-LLF	1.28	0.0%
		Total recovery	8410	
		% rec of est source	95%	
	Replicate 2	Effluent	114	1.4%
		Source	7760	92.1%
		Top-LLF	436	5.2%
		Middle-LLF	110	1.3%
		Bottom-LLF	5.24	0.1%
		Total recovery	8430	
		% rec of est source	95%	
	Replicate 3	Effluent	80.5	1.2%
		Source	6460	96.7%
		Top-LLF	119	1.8%
		Middle-LLF	20	0.3%
		Bottom-LLF	3.8	0.1%
		Total recovery	6680	
		% rec of est source	76%	

* Estimated mass of energetic compounds in source soil.

† Percent recovery of estimated mass initially present in source soil.

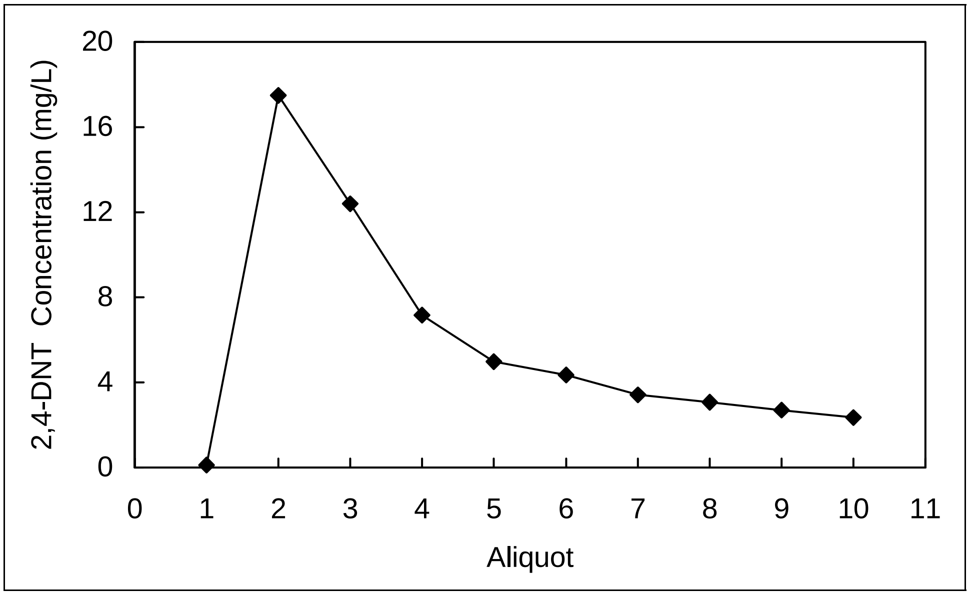


Figure 4. 2,4-DNT effluent concentration (mg/L) from columns with laboratory-fortified source soils contaminating M1 propellant residue.

M1 Composition: 155-mm Howitzer Propellant

Figure 4 shows the effluent concentrations of 2,4-DNT from the column experiment with the M1 propellant laboratory-fortified source soil. Columns with the range soil containing 105-mm howitzer propellant residues produced no detectable concentrations of 2,4-DNT in the effluent or the LLF media portions (Table 6). Therefore, there was no evidence that 2,4-DNT was leached from the range soil, a finding that is consistent with no detectable levels in groundwater at Camp Edwards, Massachusetts (Clausen et al. 2004). The explanation for this discrepancy is the same as given above, i.e., grinding pieces of propellant with sand created a lot more surface area than that present on the weathered propellant residues deposited at the training range.

Table 6. M1 residue source soil. Mass (µg) of 2,4-DNT in column effluent and portions of column media.

		Portion	Mass (µg) 2,4-DNT	% of total 2,4-DNT recovery
Sample	**Laboratory prepared**	Total source mass*	2520	
		Effluent	564	25.8%
		Source	1580	72.4%
		Top-LLF	22.2	1.0%
		Middle-LLF	8.22	0.4%
		Bottom-LLF	9.4	0.4%
		Total recovery	2180	
		% rec of est source†	87%	
Range soil	**Replicate 1**	Total source mass*	200	
		Effluent	0.01	0.0%
		Source	262	100.0%
		Top-LLF	0.01	0.0%
		Middle-LLF	0.01	0.0%
		Bottom-LLF	0.01	0.0%
		Total recovery	262	
		% rec of est source	131%	
	Replicate 2	Effluent	0.01	0.0%
		Source	47	99.9%
		Top-LLF	0.01	0.0%
		Middle-LLF	0.01	0.0%
		Bottom-LLF	0.01	0.0%
		Total recovery	47	
		% rec of est source	24%	
	Replicate 3	Effluent	0.01	0.0%
		Source	796	100.0%
		Top-LLF	0.01	0.0%
		Middle-LLF	0.01	0.0%
		Bottom-LLF	0.01	0.0%
		Total recovery	796	
		% rec of est source	398%	

* Estimated mass of energetic compounds in source soil.

† Percent recovery of estimated mass initially present in source soil.

The effluent NG and 2,4-DNT concentrations and their respective percentage of total mass for laboratory-prepared M7 and M1 source soil columns showed the same trend as the aqueous dissolution study. That is, more NG was released than 2,4-DNT (Tables 5 and 6). In this case, the surface area should have been fairly consistent since both were ground with sand for the same amount of time.

Profile samples collected at active 105-mm howitzer firing points have shown that, depending on the presence or absence of surface vegetation, 2,4-DNT may or may not be present in the subsurface (Walsh et al. 2005). At a non-vegetated firing point, concentrations of 2,4-DNT present at a depth of 15–20 cm were approximately an order of magnitude lower than at the surface; 2,4-DNT wasn't detected at this interval on a vegetated range (Walsh et al. 2005). Additional work is needed to explain this apparent discrepancy between laboratory and field results.

5 SUMMARY

In this laboratory study, energetic compounds dissolved rapidly from a soil containing weathered crystals of Composition B. High concentrations of RDX and HMX along with moderate levels of TNT and low levels of the AmDNTs eluted from a column containing source soil from an active training range that is a potential point source for groundwater contamination. Moreover, the levels of TNT and AmDNTs eluting decreased rapidly, due most likely to an increase in microbiological activity. Mass balance estimates for the column elution experiment indicated RDX and HMX were conservative, i.e., these two compounds were not degraded whereas TNT was influenced by transformation.

The dissolution of NG or 2,4-DNT was not rapid from soils laden with propellant residues collected at firing positions on active training ranges. These two energetic residues are imbibed in a NC polymer matrix, which inhibits the rate of dissolution, particularly for the particle size range that is deposited during military training exercises. Both the dissolution experiment and the column elution experiments showed NG to be more readily leached from the M7 propellant composition than 2,4-DNT from the M1 composition. Because of this slow rate of release of NG and 2,4-DNT from propellant compositions and the dependency on particle size deposited during training exercises, laboratory-based studies should use range soils laden with propellant residues to study their fate and transport.

REFERENCES

Brannon, J.M., and J.C. Pennington (2002) Environmental fate and transport process descriptors for explosives. U.S. Army Engineer Research and Development Center, Environmental Laboratory, Vicksburg, Mississippi, Technical Report ERDC/EL TR-02-10.

Clausen, J., J. Robb, D. Curry, and N. Korte (2004) A case study of contaminants on military range: Camp Edwards, Massachusetts, USA. *Environmental Pollution*, **129**:13–21.

Hewitt, A.D., and M.E. Walsh (2003) On-site processing and subsampling of surface soils samples for the analysis of explosives. U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, Technical Report ERDC/CRREL TR-03-14.

Hewitt, A.D., T.F. Jenkins, T.A. Ranney, J.A. Stark, M.E. Walsh, S. Taylor, M.R. Walsh, D.J. Lambert, N.M. Perron, N.H. Collins, and R. Karn (2003) Estimates for explosives residues from the detonation of Army munitions. U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, Technical Report ERDC/CRREL TR-03-16.

Jenkins, T.F., T.A. Ranney, P.H. Miyares, N.H. Collins, and A.D. Hewitt (2000a) Use of surface snow sampling to estimate the quantity of explosive residues resulting from land mine detonations. U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, Technical Report ERDC/CRREL TR-00-12.

Jenkins, T.F., T.A. Ranney, M.E. Walsh, P.H. Miyares, A.D. Hewitt, and N.H. Collins (2000b) Evaluating the use of snow-covered ranges to estimate explosives residues that result from detonation of Army munitions. U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, Technical Report ERDC/CRREL TR-00-15.

Jenkins, T.F., J.C. Pennington, T.A. Ranney, T.E. Berry, P.H. Miyares, M.E. Walsh, A.D. Hewitt, N.M. Perron, L.V. Parker, C.A. Hayes, and E. Wahlgren (2001) Characterization of explosives contamination at military firing ranges. U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hanpshire, Technical Report ERDC/CRREL TR-01-5.

Jenkins, T.F., C. Bartolini, and T.A. Ranney (2003) Stability of CL-20, TNAZ, HMX, RDX, NG, and PETN in moist, unsaturated soil. U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, Technical Report ERDC/CRREL TR-03-7.

Jenkins, T.F., T.A. Ranney, A.D. Hewitt, M.E. Walsh, and K.L. Bjella (2004a) Representative sampling for energetic compounds at an antitank firing range. U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, Technical Report ERDC/CRREL TR 04-7.

Jenkins, T.F., A.D. Hewitt, T.A. Ranney, C.A. Ramsey, D.J. Lambert, K.L. Bjella, and N.M. Perron (2004b) Sampling strategies near a low-order detonation and a target at an artillery impact area. U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, Technical Report ERDC/CRREL TR-04-14.

Jenkins, T.F., A.D. Hewitt, M.E. Walsh, T.A. Ranney, C.A. Ramsey, C.L. Grant, and K.L. Bjella (2005) Representative sampling for energetic compounds at military training ranges. *Journal of Environmental Forensics*, **6**: 45–55.

Kayser, E.G., and N.E. Burlinson (1988) Migration of explosives in soil: Analysis of RDX, TNT, and tetryl from a 14C lysimeter study. *Journal of Energetic Materials*, **6**: 45–71.

Major, M. (1999) Biological degradation of explosives. In *Bioremediation of Contaminated Soils*. American Society of Agronomy, Madison, Wisconsin, *Agronomy Monograph*, **37**: 112–131.

McCormick, N.G., F.E. Feeherry, and H.S. Levinson (1976) Microbial transformation of 2,4,6-trinitrotoluene and other nitroaromatic compounds. *Applied Environmental Microbiology*, **31**: 949–958.

Pennington, J.C., K.F. Myers, W.M. Davis, T.J. Olin, T.A. McDonald, C.A. Hayes, and D.M. Townsend (1995) Impacts of sorption on the in-situ bioremediation of explosives-contaminated soils. U.S. Army Corps of Engineers, Waterways Experiment Station, Vicksburg, Mississippi, Technical Report IRP-95-1.

Pennington, J.C., T.F. Jenkins, P.H. Miyares, M.E. Walsh, A.D. Hewitt, N. Perron, T.A. Ranney, J. Lynch, J.J. Delfino, and C.A. Hayes (2001) Distribution and fate of energetics on DoD test and training ranges: Interim Report 1. U.S. Army Engineer Research and Development Center, Environmental Laboratory, Vicksburg, Mississippi, Technical Report ERDC/EL TR-01-13.

Pennington, J.C., T.F. Jenkins, G. Ampleman, S. Thiboutot, J.M. Brannon, J. Lynch, T.A. Ranney, J. Stark, M.E. Walsh, J. Lewis, C.A. Hayes, J.E. Mirecki, A.D. Hewitt, N. Perron, D. Lambert, J. Clausen, and J.J. Delfino (2002) Distribution and fate of energetics on DoD test and training ranges: Interim Report 2. U.S. Army Engineer Research and Development Center, Environmental Laboratory, Vicksburg, Mississippi, Technical Report ERDC/EL TR-02-8.

Pennington, J.C., T.F. Jenkins, G. Ampleman, S. Thiboutot, J.M. Brannon, J. Lewis, J.E. DeLaney, J. Clausen, A.D. Hewitt, M.A. Hollander, C.A. Hayes, J.A. Stark, A. Marois, S. Brochu, H.Q. Dinh, D. Lambert, A. Gagnon, M. Bouchard, R. Martel, P. Brousseau, N.M. Perron, R. Lefebvre, W. Davis, T.A. Ranney, C. Gauthier, S. Taylor, and J. Ballard (2003) Distribution and fate of energetics on DoD test and training ranges: Interim Report 3. U.S. Army Engineer Research and Development Center, Environmental Laboratory, Vicksburg, Mississippi, Technical Report ERDC/EL TR-03-2.

Pennington, J.C., T.F. Jenkins, G. Ampleman, S. Thiboutot, J. Brannon, J. Clausen, A.D. Hewitt, S. Brochu, P. Dube, J. Lewis, T.A. Ranney, D. Faucher, A. Gagnon, J.A. Stark, P. Brousseau, C.B. Price, D. Lambert, A. Marois, M. Bouchard, M.E. Walsh, S.L. Yost, N.M. Perron, R. Martel, S. Jean, S. Taylor, C.A. Hayes, J. Ballard, M.R. Walsh, J.E. Mirecki, S. Downe, N.H. Collins, B. Porter, and R. Karn (2004) Distribution and fate of energetics on DoD test and training ranges: Interim Report 4. U.S. Army Engineer Research and Development Center, Environmental Laboratory, Vicksburg, Mississippi, Technical Report ERDC/EL TR-04-4.

Phelan, J.M., S.W. Webb, J.V. Romero, J.L. Barnett, F. Griffin, and M. Eliassi (2003) Measurement and modeling of energetic materials mass transfer to soil pore water—Project CP-1227, Sandia Report 2003-0153.

Selim, M.H., and I.K. Iskandar (1994) Sorption-desorption and transport of TNT and RDX in soils. U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, CRREL Report 94-7.

Taylor, S., A. Hewitt, J. Lever, C. Hayes, L. Perovich, P. Thorne, and C. Daghlian (2004) TNT particle size distributions from detonated 155-mm howitzer rounds. *Chemosphere*, **55**: 357–367.

Thorne, P.G., and D.C. Leggett (1997) Hydrolyic release of bound residues from composted soil contaminated with 2,4,6-trinitrotoluene. *Environmental and Toxicological Chemisty*, **16**: 1132–1134.

Thiboutot, S., G. Ampleman, A. Marois, A. Gagnon, M. Bouchard, A. Hewitt, T.F. Jenkins, M.E. Walsh, and K. Bjella (2004) Environmental condition of surface soils, CFB GageTown training area: Delineation of the presence of munitions-related residues (Phase III, Final Report). Defense Research and Development Canada Valcartier. DRDC Valcartier TR 2004-205.

U.S. EPA (1994) Method 8330: Nitroaromatics and nitramines by HPLC. In *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington D.C., SW-through Update 4b (www.epa.gov.sw-846).

U.S. EPA (2000) Administrative Order for Massachusetts Military Reservation Training Range and Impact Area Response Action. EPA Docket No. SDWA-1-2000-0014. Region 1, Boston, Massachusetts.

Walsh, M.E., C.M. Collins, C.H. Racine, T.F. Jenkins, A.B. Gelvin, and T.A. Ranney (2001) Sampling for explosives residues at Fort Greely, Alaska: Reconnaissance visit July 2000. U.S. Army Engineer Research and Development Center, Hanover, New Hampshire, Technical Report ERDC/CRREL TR-01-15.

Walsh, M.E., C.A. Ramsey, and T.F. Jenkins (2002) The effect of particle size reduction by grinding on subsampling variance for explosives residues in soil. *Chemosphere*, **49**: 1267–1273.

Walsh, M.E., C.M. Collins, A.D. Hewitt, M.R. Walsh, T.F Jenkins, J. Stark, A. Gelvin, T. Douglas, N. Perron, D. Lambert, R. Bailey, and K. Myers (2004) Range characterization studies at Donnelly Training Area, Alaska 2001 and 2002. U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, Technical Report ERDC/CRREL TR-04-3.

Walsh, M.E., C.A. Ramsey, C.M. Collins, A.D. Hewitt, M.R. Walsh, and K. Bjella (2005) Collection methods and laboratory processing of samples from Donnelly Training Area Firing Points, Alaska, 2003, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, Technical Report ERDC/CRREL TR-05-5.

APPENDIX A. CONCENTRATION ESTIMATES FOR COLUMN EFFLUENT AND MEDIA PORTIONS.

Table A1. Composition B source soil.

	Effluent							Media portions							
Column	**Aliquot**	**Vol. (mL)**	**HMX (mg/L)**	**RDX (mg/L)**	**TNT (mg/L)**	**2AmDNT (mg/L)**	**4AmDNT (mg/L)**	**Media**	**Weight (g)**	**Solvent vol. (mL)**	**HMX (µg/g)**	**RDX (µg/g)**	**TNT (µg/g)**	**2AmDNT (µg/g)**	**4AmDNT (µg/g)**
Replicate 1	1	6.53	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	Source	9.18	20	58.6	438	73.2	1.37	1.53
	2	9.52	0.810	16.4	15.5	0.55	0.29	Top	12.72	20	0.978	6.92	0.660	0.090	0.110
	3	9.61	2.05	31.8	26.3	0.74	1.01	Mid	15.88	20	0.460	4.99	0.565	0.072	nd
	4	9.71	2.16	29.8	16.7	0.76	1.03	Bottom	14.7	20	0.411	4.80	0.555	0.069	nd
	5	9.65	2.15	28.4	11.9	0.63	0.83								
	6	9.67	2.09	27.4	7.72	0.50	0.72								
	7	9.61	2.28	29.7	6.48	0.44	0.65								
	8	9.80	2.17	26.7	5.50	0.39	0.58								
	9	9.76	1.94	23.7	4.05	0.33	0.50								
	10	9.76	1.64	22.2	2.80	0.28	0.41								
	11	9.71	1.82	24.1	2.88	0.25	0.36								
	12	9.79	1.78	21.7	2.39	0.23	0.33								
Replicate 2	1	6.53	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	Source	9.41	20	39.5	261	8.7	1.32	1.15
	2	9.40	0.600	14.5	14.0	0.57	0.26	Top	13.56	20	1.24	5.91	0.226	0.080	0.080
	3	9.37	2.12	30.8	25.4	0.7	0.93	Mid	13.69	20	0.454	4.97	0.210	0.067	nd
	4	9.67	2.10	28.9	14.1	0.71	0.95	Bottom	16.52	20	0.390	4.48	0.180	0.054	0.070
	5	9.82	2.03	28.2	8.65	0.58	0.78								
	6	9.71	1.95	25.4	4.88	0.45	0.66								
	7	9.86	2.17	27.6	3.57	0.40	0.61								
	8	9.72	1.94	23.6	2.64	0.34	0.51								
	9	9.84	1.76	22.4	1.95	0.29	0.43								
	10	9.68	1.67	21.9	1.33	0.26	0.37								
	11	9.71	1.80	22.3	1.14	0.22	0.32								
	12	9.75	1.71	20.4	0.86	0.20	0.29								

Table A1 (cont'd).															
	Effluent							Media portions							
Column	**Aliquot**	**Vol. (mL)**	**HMX (mg/L)**	**RDX (mg/L)**	**TNT (mg/L)**	**2AmDNT (mg/L)**	**4AmDNT (mg/L)**	**Media**	**Weight (g)**	**Solvent vol. (mL)**	**HMX (µg/g)**	**RDX (µg/g)**	**TNT (µg/g)**	**2AmDNT (µg/g)**	**4AmDNT (µg/g)**
Replicate 3	1	6.43	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	Source	9.00	20	36.4	322	4.70	1.33	1.44
	2	9.37	0.63	15.1	15.0	0.61	0.27	Top	15.4	20	0.875	9.01	0.052	0.060	0.090
	3	9.42	2.09	31.2	27.3	0.73	0.99	Mid	12.9	20	0.451	4.76	0.086	0.053	0.090
	4	9.62	2.07	29.4	14.4	0.74	0.97	Bottom	16.2	20	0.394	4.32	0.062	0.051	0.070
	5	9.84	1.94	28.1	8.84	0.59	0.80								
	6	9.68	2.04	26.7	5.48	0.45	0.66								
	7	9.83	2.39	30.6	4.17	0.40	0.60								
	8	9.72	2.05	25.4	2.73	0.32	0.47								
	9	9.79	1.75	23.1	1.90	0.26	0.39								
	10	9.75	1.76	22.8	1.30	0.22	0.32								
	11	9.81	1.78	22.5	1.17	0.19	0.27								
	12	9.78	1.70	19.6	0.82	0.16	0.24								

Table A2. M1 propellant source and laboratory-prepared soils.							
Aliquot	**Volume (mL)**	**2,4-DNT (mg/L)**		**Position**	**Weight (g)**	**Solvent volume (mL)**	**2,4-DNT (µg/g)**
M1: Range residue source soil							
Replicate 1: Effluent				**Replicate 1: Media portions**			
1	7.20	< 0.020		Source	9.67	20	27.1
2	9.69	< 0.020		Top	10.47	20	< 0.04
3	9.75	< 0.020		Mid	13.26	20	< 0.04
4	9.87	< 0.020		Bottom	17.96	20	< 0.04
5	9.86	< 0.020					
6	9.83	< 0.020					
7	9.87	< 0.020					
8	9.84	< 0.020					
9	9.66	< 0.020					
10	9.80	< 0.020					
Replicate 2: Effluent				**Replicate 2: Media portions**			
1	8.06	< 0.020		Source	10.00	20	4.7
2	9.78	< 0.020		Top	13.38	20	< 0.04
3	9.75	< 0.020		Mid	14.25	20	< 0.04
4	9.75	< 0.020		Bottom	12.43	20	< 0.04
5	9.83	< 0.020					
6	9.88	< 0.020					
7	9.77	< 0.020					
8	9.80	< 0.020					
9	9.81	< 0.020					
10	9.73	< 0.020					

Table A2 (cont'd).							
Aliquot	Volume (mL)	2,4-DNT (mg/L)		Position	Weight (g)	Solvent volume (mL)	2,4-DNT (µg/g)
M1: Range residue source soil (cont'd)							
Replicate 3: Effluent				Replicate 3: Media portions			
1	8.06	< 0.020		Source	9.3	20	85.6
2	9.78	< 0.020		Top	14.5	20	< 0.04
3	9.75	< 0.020		Mid	15.53	20	< 0.04
4	9.75	< 0.020		Bottom	11.65	20	< 0.04
5	9.83	< 0.020					
6	9.88	< 0.020					
7	9.77	< 0.020					
8	9.80	< 0.020					
9	9.81	< 0.020					
10	9.73	< 0.020					
M1: Laboratory-prepared							
Effluent				Media portions			
1	8.52	0.125		Source	7.97	20	198
2	9.76	17.5		Top	13.35	20	1.66
3	9.80	12.4		Mid	12.36	20	0.665
4	9.59	7.17		Bottom	16.38	20	0.574
5	9.54	4.97					
6	9.75	4.34					
7	9.82	3.41					
8	9.86	3.07					
9	9.79	2.69					
10	9.80	2.36					

Table A3. M7 propellant source and laboratory-prepared soils.							
Aliquot	**Volume (mL)**	**NG (mg/L)**		**Position**	**Weight (g)**	**Solvent volume (mL)**	**NG (µg/g)**
M7: Range residue source soil							
Replicate 1: Effluent				**Replicate 1: Media portions**			
1	8.06	< 0.05		Source	8.68	20	922
2	9.59	6.86		Top	17.22	20	15.0
3	9.70	4.86		Mid	9.8	20	1.68
4	9.77	1.34		Bottom	14.07	20	0.091
5	9.77	0.43					
6	9.90	0.165					
7	9.79	< 0.05					
8	9.83	0.109					
9	9.74	< 0.05					
10	9.76	< 0.05					
Replicate 2: Effluent				**Replicate 2: Media portions**			
1	7.73	< 0.05		Source	8.19	20	948
2	9.74	6.3		Top	11.31	20	38.6
3	9.73	3.1		Mid	14.6	20	7.56
4	9.69	0.779		Bottom	14.68	20	0.357
5	9.84	0.335					
6	9.89	0.433					
7	9.76	0.358					
8	9.72	0.381					
9	9.79	0.068					
10	9.82	< 0.05					

Table A3 (cont'd).							
Aliquot	**Volume (mL)**	**NG (mg/L)**		**Position**	**Weight (g)**	**Solvent volume (mL)**	**NG (µg/g)**
M7: Range residue source soil (cont'd)							
Replicate 3: Effluent				**Replicate 3: Media portions**			
1	8.06	< 0.05		Source	10.51	20	615
2	9.78	5.78		Top	10.76	20	11.1
3	9.75	2.17		Mid	12.99	20	1.54
4	9.75	0.29		Bottom	15.29	20	0.249
5	9.83	< 0.05					
6	9.88	< 0.05					
7	9.77	< 0.05					
8	9.80	< 0.05					
9	9.81	< 0.05					
10	9.73	< 0.05					
M7: Laboratory prepared							
Effluent				**Media portions**			
1	8.09	2.25		Source	8.51	20	124
2	9.88	283		Top	13.92	20	33.3
3	9.87	77.7		Mid	12.98	20	0.505
4	9.65	19.6		Bottom	14.58	20	0.649
5	9.69	9.32					
6	9.74	6.96					
7	9.76	4.51					
8	9.67	4.22					
9	9.64	3.67					
10	9.63	2.98					

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YY)*
July 2005

2. REPORT TYPE
Technical Report

3. DATES COVERED *(From - To)*

4. TITLE AND SUBTITLE

Elution of Energetic Compounds from Propellant and Composition B Residues

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

Alan D. Hewitt and Susan R. Bigl

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

U.S. Army Engineer Research and Development Center
Cold Regions Research and Engineering Laboratory
72 Lyme Road
Hanover, New Hampshire 03755

8. PERFORMING ORGANIZATION REPORT

ERDC/CRREL TR-05-13

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U.S. Army Environmental Center
Aberdeen Proving Ground
Maryland 21010

10. SPONSOR / MONITOR'S ACRONYM(S)

11. SPONSOR / MONITOR'S REPORT NUMBER(S)

SFIM-AEC-AT-CR-2005047

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

Available from NTIS, Springfield, Virginia 22161.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Surface soils from two firing points, an artillery impact range, and soils fortified with propellants were evaluated in column elution experiments assessing the release of energetic compounds from melt-cast crystalline explosives and nitrocellulose-based polymeric propellant formulations. Soils obtained from active military ranges were collected at locations identified as potential source zones for energetic residues. The laboratory columns contained 30 g of a silty-sand loam beneath 5.0 g of soil laden with energetic compounds. For 10 or 12 consecutive days, 10 mL of water was eluted through each of the columns. HMX, RDX, and TNT were quickly leached from a soil laden with Composition B residues that had been obtained where an artillery projectile had partially detonated. In contrast, neither 2,4-DNT nor NG were readily released from surface soils laden with propellant residues deposited from the firing of 105-mm howitzers and Light Anti-Armor Weapons (LAW), respectively. A soil prepared by grinding pieces of 105-mm howitzer and LAW rocket propellants with a sand matrix released much greater concentrations of 2,4-DNT and NG than residue-laden soils from firing points. Both the composition of energetic formulations (crystalline vs. polymeric) and physical state of propellant residues deposited at firing points play important roles in the fate and transport of energetic compounds.

15. SUBJECT TERMS

2,4-DNT	Energetic residues	RDX
Column elution study	NG	TNT
Composition B	Propellant	Transport

16. SECURITY CLASSIFICATION OF:

a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
U	U	U	U	38	19b. TELEPHONE NUMBER *(include area code)*